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TANNIN-FORMALDEHYDE ADHESIVES

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INTRODUCTION

1. Phenolic groups occur in tannins, many of which may be reacted with formaldehyde to form resins. Some of these have potential use in the manufacture of highly reactive waterproof adhesives. In Australia, commercial tannins offer a substantial cost advantage over phenol, which is the most important raw material for waterproof plywood adhesives.

2. Some time ago the Chemical Research Laboratories examined tannins as a possible base for adhesives,[2,3] while more recently the Division of Forest Products has investigated the properties of a number of tannins as a base for waterproof adhesives. This report outlines some aspects of the investigations carried out at the Division of Forest Products.

THE TANNIN-FORMALDEHYDE REACTION

3. Mangrove (Rhizophora and Bruguiera spp.), wattle (Acacia mollissima) and radiata (Pinus radiata) bark extracts react readily with formaldehyde to form resins. Under appropriate conditions the reaction takes place comparatively rapidly at ambient temperatures, but in gluing best results have been obtained at elevated temperatures.

4. These tannins differ in rate of reaction with formaldehyde, as is shown by time taken for tannin solutions to form a gel under uniform conditions. At 60°C and at an arbitrary pH 6.0 the gelation times for radiata, mangrove, and wattle tannin were found to be 2.6, 12.5 and 55.7 minutes respectively.

5. The rate at which these tannins react with formaldehyde varies with pH, and is accelerated by certain soluble salts.[4] In the case of wattle tannin, when the gelation time is plotted against pH over a range of about 1.5 - 7.0, a maximum (region of lowest reactivity) is found at pH 3.0 - 3.5. Also the gelation time is reduced (reactivity increased) by a number of soluble salts, some of the most effective being salts of zinc, copper, chromium and aluminium. In these investigations the effects of the various salts

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[2] L.K. Dalton, Tannin-formaldehyde resins as adhesives for wood, Aust. J. Appl. Sci. 1, 54 (1950).
[3] L.K. Dalton, Resins from sulphited tannins as adhesives for wood, Aust. J. Appl. Sci. 4, 136 (1953).
[4] Plomley, K.F., The effect of soluble salts on the gelation of tannin-formaldehyde, Aust. J. Appli. Sci. 10, 494-497 (1959).

were compared at a concentration of 10 per cent of the dry wattle tannin. Later work has shown that less than 2 per cent of the more effective salts can produce a substantial acceleration of gelation.

TANNIN-FORMALDEHYDE ADHESIVES FOR PLYWOOD MANUFACTURE

Adhesive Properties of Different Tannins

6. Early studies on mangrove tannin[5] showed that by using simple formulation it was possible to prepare adhesives which in shear strength tests complied with the waterproof requirements of the Australian Standard for synthetic resin adhesives for plywood. Values for wood failure, however, were uniformly low and could not be regarded as satisfactory. It was found that waterproof adhesives giving high values for shear strength and wood failure and able to withstand immersion in boiling water for 72 hours, could be prepared by adding a small proportion of a suitably formulated phenolic resin.

7. Two other commercial tannin extracts, viz. wattle and wandoo (Eucalyptus wandoo and E. accedens) were also examined. Table 1 shows the differences in adhesive properties between the three extracts and also the effect on the quality of the bond with klinki pine (Araucaria klinkii) of adding varying amounts of fortifying resin.

Table 1

EFFECT OF ADDING FORTIFYING RESIN[a] ON BONDS OF KLINKI PINE USING TANNIN-BASED ADHESIVES

Amount of fortifying resin (%) (dry solids basis)	Mangrove		Wattle		Wandoo	
	Tested dry	Tested wet after 6-hr boil	Tested dry	Tested wet after 72-hr boil	Tested dry	Tested wet after 72-hr boil
0	309[b]- 11[c]	120[b]- 0[c]	290- 47	236-100	165- 5	0- 0
10	278 - 24	200 - 35	390- 97	290-100	301-52	150-21
20	314 - 50	203 - 56	481-100	296-100	369-96	248-83
30	340 -100	305 -100	423-100	300-100	382-82	266-93

[a] Phenol formaldehyde resin used with mangrove tannin; with the other two species a resorcinol phenol formaldehyde was used.

[b] Glue shear strength (lb/sq in) - Tested according to Aust. Stand. Spec. No. K.88, 1952, (min mean failing load = 200 lb).

[c] Wood failure (%).

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[5] Plomley, K.F., Gottstein, J.W., and Hillis, W.E., Tannin-formaldehyde adhesives, C.S.I.R.O. For. Prod. Newsl. 234, 6-8 (1957).

Effect of Alkali on Adhesive Properties.

8. When developing a formulation for a mangrove tannin adhesive, it was observed that addition of highly alkaline commercial phenolic resins to the tannin solution produced a mix of unsatisfactory physical characteristics. This was due partly to precipitation of the commercial phenolic resin at the lower pH and partly to the effect of the alkali on the tannin.

9. Wattle and radiata tannins do not show such marked changes on the addition of alkali as does mangrove tannin. However, recent investigations have demonstrated that the use of alkaline glue mixes or of alkaline tannin extracts may result in an inferior bond. Under alkaline conditions the reactivity of the tannin is high and the solubility of paraformaldehyde (the form in which formaldehyde is generally added to the adhesive) is increased, leading to premature reaction of the materials. It was also found that exposure of the tannin to moderately high pH for 72 hours resulted in a reduction in the bond quality observed after immersion in boiling water for 6 hours.

Bond Strength of Wattle Tannin Adhesives with Different Veneers.

10. Comparatively simple tannin-formaldehyde mixes are effective for bonding plywood. A typical formulation consists essentially of a concentrated solution of the tannin in water adjusted to a suitable pH, with paraformaldehyde as the cross-linking agent, and with or without a small amount of fortifying resin. Wood filler is also added to minimize loss of adhesive through penetration and to provide gap-filling properties.

11. The bond strength of wattle tannin formulations with different commercial veneers has been investigated. Some typical results are given in Table 2 showing that wattle tannin without fortifying resin can produce a satisfactory bond with some species of veneers, but with others a small addition of a fortifying resin is necessary. Because of the variation in surface uniformity and absorptivity of veneers, and the brittle nature of the tannin-formaldehyde resin, the addition of wood flour is necessary with all mixes. The addition of fortifying resin is probably desirable with most species in order to make certain of consistently satisfactory bond quality, although unfortified wattle tannin may be generally suitable for producing a low-cost bond with high, but not necessarily maximum strength.

12. A number of trials of wattle tannin adhesives have been made under factory conditions. The results obtained with rotary peeled veneers have confirmed laboratory experience, which indicates that tannin-formaldehyde is suitable for bonding a number of commercial veneers. So far no failures have been experienced, although, because of dark colour and a tendency to penetrate, tannin adhesives are not at present recommended for bonding thin decorative face veneers.

TANNIN-FORMALDEHYDE ADHESIVES FOR BONDING PARTICLE BOARD.

13. Although investigations have been largely concentrated on the development of adhesives for plywood, some exploratory tests have been carried out with wattle tannin as a binding agent for wood particle board. These indicate that a satisfactory board can be prepared from Pinus radiata chips and unfortified wattle tannin

Table 2

BOND STRENGTH OF WATTLE TANNIN ADHESIVE FORMULATIONS WITH DIFFERENT VENEER SPECIES

Veneer Species	Concentration of Fortifying Resin (%)					
	0		10		20	
	Tested dry	Tested wet after 72-hr boil	Tested dry	Tested wet after 72-hr boil	Tested dry	Tested wet after 72-hr boil
Hoop pine[a]	388[f]-93[g]	250-92	370- 97	305- 86	362- 92	290-90
Borneo cedar[b]	293 -88	233-87	321-100	302-100	309- 92	307-94
Ramin[c]	314 -62	259-73	356- 63	274- 64	373-100	238-65
Coachwood[d]	347 -43	300-80	428- 87	262- 95	420- 89	340-98
Mountain ash[e]	330 -91	248-99	324- 71	241- 98	344- 93	250-98

[a] *Araucaria cunninghamii*; [b] *Shorea* sp.; [c] *Gonystylus* sp.;

[d] *Ceratopelum apetalum*; [e] *Eucalyptus regnans*;

[f] Shear strength (lb/sq in); [g] Wood failure (%).

adhesive. In this application, however, the colour of the adhesive may limit its usefulness unless the surface of the board is to be veneered or otherwise covered. In addition, deficiency in tackiness can have an undesirable effect in board forming.

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